PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for Hardening the Surfaces of Organic Synthetic Resins

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for hardening the surfaces of organic synthetic resins.

Surfaces of synthetic resins can be hardened by vapour deposition of SiO_x in which x has a value of about 1 to 2, in a high vacuum (10^{-4} to 10^{-6} mm Hg) and in the presence of oxygen. For example, W. Reichelt mentions in his paper "Problems bei der Herstellung dünner Schichten", published in "Vakuum Technik", vol. 15, 1966, No. 1, pages 1—8, on page 6, left-hand column, that it is possible to produce (SiO_2 layers) in this way on polycarbonates and methacrylic resins, and such layers may be surprisingly thick (about 2 to 5 μ) and may initially adhere remarkably well, although the thermal expansion of these materials is substantially greater than that of the SiO_2 layers. Such surface-hardening layers which may be glass-clear and transparent, are primarily intended to render the synthetic materials scratch resistant.

It has been found that the adhesion of such hardening layers on methacrylic resins disappears sooner or later, but that they are substantially more stable on polycarbonates; however, even then these hardening layers do not withstand severe weather conditions, for example the Weather-O-Meter test in which spraying with water takes place at regular time intervals at constantly changing temperatures and under the action of strong ultraviolet irradiation, or prolonged tests for scratch resistance of the surface.

The present invention provides an improved process for producing an organic synthetic resin having a hardened surface, by vapour deposition of SiO_x (in which x has a value of from 1 to 2) in a high vacuum and preferably in the presence of oxygen until a layer thickness of approximately 2 to 5 μ is achieved. The product has a surface hardened by means of a hardening layer which satisfies even high requirements of resistance to weather and scratching. This process is characterised by the use of synthetic resins which do not soften appreciably in the course of the vapour-deposition, whose content of components with a vapour pressure of more than 10^{-5} mm Hg at 120°C is not appreciable as hereinafter defined, and whose surface to be treated is not covered with more than 30% of a monomolecular layer of organic foreign substances. It is moreover frequently expedient to discharge the synthetic resins electrostatically before the vapour-deposition. The process is also characterised in that SiO_2 is evaporated by means of an electron beam vaporizer source (for example in known manner), but at an energy density of 5 to 15 kw/sq.cm, an effective evaporation surface of 0.3 to 0.6 sq. cm and a partial SiO_x pressure of at least 1×10^{-2} mm Hg (measured in the vapour jet with a thermoelectric manometer at a distance of 25 cm from the centre of the evaporating SiO_2 surface) and that the vapour deposition is carried out while the object is substantially steadily moved in the vapour jet or the electron beam vaporizer source is moved in such a manner that at least 40 preferably at least 50, successive layers are vapour-deposited on the surface of the

synthetic resin at an average condensation rate of SiO_x of approximately 90 to 110 Å/sec.

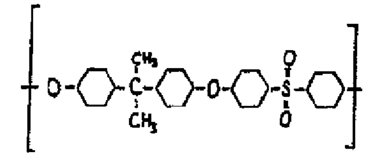
The synthetic resins to be used must not soften appreciably during the vapour-deposition, for example at temperatures up to 120° C to which at least the surfaces of the objects may be heated during the treatment, and their content of components with a vapour pressure of more than 10^{-5} mm Hg at 120°C must not be appreciable; this eliminates all those synthetic resins whose softening point is too low and which still contain volatile components, such as monomers, plasticisers, solvents, water and the like.

It is preferred to carry out the process in a vacuum of from 10^{-4} to 10^{-6} mm Hg.

The content of non-volatile components is regarded as not appreciable when an increase in the rise in pressure, compared with a blank test, over 1 sq.m of the surface of the synthetic resin during storage at 120°C and an initial pressure of 10^{-5} mm Hg in a closed vessel of not more than 100 liters capacity, is no longer measurable.

If necessary, the synthetic resins are pretreated immediately before the vapour-deposition in order to remove such components, for example by being heated in a high vacuum drier at a minimum temperature of 120°C until all volatile components have been removed. It is not sufficient to free only the external layers of the synthetic resin from these components: if components of this type remain in the interior, they gradually diffuse into the external layer causing the adhesion of the hardening layer to disappear sooner or later. On the other hand, a subsequent reabsorption of moisture is not detrimental.

A list of some synthetic resins which are suitable for the process, possibly after the pretreatment described immediately above, includes the following: linear thermoplastic polyesters which are free from plasticiser, such as terephthalic acid ethylene glycol polyester; polycarbonates with a sufficiently high softening point, especially those based on aromatic dihydroxy compounds, in particular on bis - (hydroxyphenyl) - alkanes, bis - (hydroxyphenyl) - sulphones, bis - (hydroxyphenyl) - ethers, bis - (hydroxphenyl) - sulphides and the like; linear, thermoplastic polyarylene polyethers, for example, the polyether polysulphone with structural units of the formula:—



or the polyether of 2,6 - dimethyl-phenol; and also cross-linked synthetic materials, such as epoxide resins hardened by acid anhydrides or amines, and polymeric diethylene glycol-bis-allyl carbonate.

The process can be used, for example, for treating moulded articles, such as foils, plates, rods, tubes, lenses and the like, made of the appropriate synthetic resin, or objects of any kind which are coated with lacquer films. The lacquer films can consist, for example, of polyurethane lacquers, ricinene/alkyd resin/aminoplast combination lacquers, epoxide resin lacquers which are hardened by acid or amine or by urea, melamine resin and isocyanate, lacquers based on epoxy esters, silicone resin lacquers, cyclised rubber lacquers, acrylic resin lacquers and the like.

Since a cover of organic foreign substances on the surface of the synthetic resin prevents the adhesion of the hardening layer, the surfaces to be treated should be free from such foreign substances to the greatest possible extent. The limit for a cover of such foreign substances which can just be tolerated, if necessary, has been established at 30% of a monomolecular layer. This means, for example, that moulded articles of synthetic resins, must have been produced without the use of release agents and the like. Even wiping of the surface with, for example, a solvent can be detrimental. Care should also be taken that as few particles of organic substances as possible settle on the surfaces. For this reason it is expedient to discharge the synthetic resins electrostatically before the vapour-deposition, for example by means of an ion spray gun. The interior of the vaporisation device should also be kept as free as possible from oil vapours which may originate from packings or from the pumps.

As mentioned above, it has also been found that the vapour-deposition itself must be carried out under certain conditions. The first requirement of this type is that SiO_2 is evaporated with an electron beam vaporiser source at an energy density of about 5 to 15 kw/sq.cm and an effective evaporation surface of SiO_2 of about 0.3 to 0.6 sq.cm. It is inevitable that a certain dissociation of SiO_2 to SiO_x takes place, x having a value of between 1 and 2. Since the oxygen split off in this process is preferably sucked off by the pumps, a sufficient supply of oxygen should normally be provided so that the material deposited as hardening layer again essentially consists of SiO_2. Otherwise more or less coloured layers would be obtained, as the light absorption of silicon increases as the degree of oxidation decreases.

Another requirement for the vapour-deposition is a minimum partial pressure of the SiO_x vapour in the vapour jet in order to overcompensate the covering of the object surface with foreign particles, for example, oil particles or residual gases, which cannot be completely avoided even with the utmost care,

during the vapour deposition by a suitable strong impact of SiO_2 particles. The partial pressure of SiO_x, measured in the vapour jet with the thermoelectric manometer at a distance of 25 cm from the centre of the evaporating SiO_2 surface, should therefore be at least 1×10^{-3} mm Hg.

Another requirement is that the surface of the object to be treated by vapour-deposition should be hit by the SiO_x jet as uniformly as possible and, if possible, at an angle of 90° in order to achieve a uniform rate of growth of the hardening layer throughout. Layers of uneven thickness are the cause of tensions and thus of a poor stability of the coating. A uniform rate of growth of the hardening layer may be achieved by constantly moving the object in the vapour jet or moving the electron beam vaporizer source.

Finally, it is also necessary that the hardening layer should grow at a certain speed. The condensation rate of SiO_x should therefore amount to between 90 and 110 Å/sec. This can be achieved by appropriately correlating the distance of the surface to be treated from the evaporating SiO_2 surface and the time of residence during which the surfaces to be treated face the SiO_x jet. Moreover, the condensation of SiO_x on the surfaces to be treated should preferably take place in at least 50 successive layers.

It has been found that the joint effect of all the aforesaid conditions is needed to give a sufficiently effectively hardened surface of a synthetic material by means of a durable coating which is resistant to scratching and weather.

The invention is illustrated by the following Example:—

EXAMPLE

A vapour-deposition device of conventional design and 500 litres capacity is fitted with a dosing valve arranged tangentially to the vacuum chamber wall and with a second dosing valve arranged at right angles to the direction of suction of the diffusion pump, for example in the vacuum chamber lid. The two valves can be so regulated that a constant preliminary pressure of about 1×10^{-4} mm Hg, measured with a Penning vacuum meter, is maintained in the vicinity of the plate valve of the diffusion pump when that pump works at fulll suction capacity.

Furthermore, a Root's pump filled with previously used diffusion pump oil is connected before the slide valve forepump. The pipe line from the forepump to the vacuum chamber is so dimensioned that any oil vapours can be deposited in the pipe line. If necessary, a molecular sieve or active charcoal filter is inserted in this pipe line.

The electron beam vaporizer source used is fitted with a hair pin cathode of the type of the so-called oblique ray guns with a ray deflection of 180°, and with a SiO_2 anode with an effective evaporation surface of 0.6 sq.cm. This anode is so devised that SiO_2 is supplied at the rate of its evaporation.

A slightly bent polycarbonate plate of $0.1\times60\times160$ cm is arranged at a distance of 40 cm from the electron beam vaporizer source.

(This plate is extruded from a commercial bisphenol A polycarbonate granulate by means of a slot die. Immediately after the extrusion it is electrostatically discharged by means of an ion spray gun and placed in a metal frame in such a manner that it is cylindrically bent with an inside height of about 10 cm. The plate is then placed without delay in the vapour-deposition device. If this is not possible, the plate is pre-treated, before being placed in the device, for at least 2 hours at 120°C and 0.1 mm Hg in a vacuum drier in whose vacuum pipe line to the pump an active charcoal filter has been inserted. Before being placed in the device, the plate is again discharged with an ion spray gun.

The vapour-deposition device is then closed and the pressure reduced to 1×10^{-5} mm Hg. The dosing valves mentioned above are then so regulated that a constant pressure of 1×10^{-4} is maintained. The electron beam vaporizer source is then passed to and fro below the surface to be treated at a uniform rate of 20 cm/sec, the cathode heating is switched on and adjusted to a current composition of about 30 Å. The high voltage is then slowly raised until the SiO_2 has been ignited and begins to evaporate. The cathode heating is then reduced as far as possible and the electron beam vaporizer source adjusted to a density of energy of about 10 kw/sq.cm of SiO_2 surface. The partial pressure of SiO_x in the vapour jet amounts to about 1×10^{-3} mm Hg, measured with a thermoelectric manometer at a distance of 25 cm from the centre of the evaporating SiO_2 surface. The mean condensation rate of SiO_x on the polycarbonate surface amounts to about 100 Å/sec.

Vapour-deposition on the polycarbonate plate is allowed to continue under these conditions for 6 minutes. During this period of time about 50 successive layers of SiO_x are deposited on the polycarbonate surface yielding a hardening layer of 3.5 μ thickness in all; this is uniform over the whole plate, of glass-clear transparency, very hard and resistant to scratch and weather.

WHAT WE CLAIM IS:—

1. A process for producing an organic synthetic resin having a hardened surface by vapour-deposition of SiO_x (wherein x has a value of from 1 to 2) in a high vacuum until a layer thickness of approximately 2 to 5 μ is achieved, in which (I) there is used as the synthetic resin a synthetic resin which

does not soften appreciably during the vapour-deposition, whose content of components with a vapour pressure of more than 10^{-5} mm Hg at 120°C is not appreciable as hereinbefore defined, and whose surface to be treated is not covered with more than 30% of a monomolecular layer of organic foreign substances, (2) SiO_2 is evaporated by means of an electron beam vaporizer source at an energy density of 5 to 15 kw/sq.cm, an effective evaporation surface of 0.3 to 0.6 sq.cm and a partial SiO_x pressure of at least 1×10^{-2} mm Hg (measured in the vapour jet with a thermoelectric manometer at a distance of 25 cm from the centre of the evaporating SiO_2 surface), and (3) the vapour-deposition takes place while the object is substantially uniformly moved in the vapour jet or the electron beam vaporizer source is moved in such a manner that at least 40 successive layers are vapour-deposited on the surfaces of the synthetic resin at a mean condensation rate of SiO_x of 90 to 110° Å/sec.

2. A process according to claim 1 in which the synthetic resin is discharged electrostatically immediately before the vapour-deposition.

3. A process according to claim 1 or 2 in which at least 50 successive layers are vapour-deposited.

4. A process according to any of claims 1—3 in which the vapour-deposition is carried out in the presence of oxygen.

5. A process according to any of claims 1—4 in which the vapour deposition is carried out in a vacuum of 10^{-4} to 10^{-6} mm Hg.

6. A process according to any of claims 1—5 in which the synthetic resin is one of those hereinbefore listed.

7. A process according to claim 1, substantially as hereinbefore described in the Example.

8. Synthetic resins having a hardened surface whenever produced by a process according to any of claims 1—7.

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